

# Long-Life Moving-Bed Zinc Titanate Sorbents

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## Abstract

Coal Fired Gasifier Combined Cycles (GCC) have both high efficiency and very low emissions. GCCs critically need a method of removing the  $H_2S$ , which is produced from the sulfur in hot coal gases. There has been extensive research on hot gas clean-up systems, focusing on the use of a zinc oxide based sorbent (e.g., zinc titanate). However, the previous sorbents show significant losses in sulfur capacity with cycling. TDA Research, Inc. (TDA) recently increased the zinc oxide content and sulfur loadings while simultaneously improving the attrition resistance. The sorbents absorb at conditions simulating a moving bed reactor for GCC (i.e., 20 atm, 482°C [900°F], and 1.2%  $H_2S$  absorptions).

We regenerate the zinc oxide sorbent at high pressure (5 atm) with high concentrations of both  $SO_2$  (10%) with  $O_2$  (4%) in the inlet of the regeneration gas. The high concentration of oxygen increases the temperature of the inlet gas and sorbent from 371°C (700°F) to 690°C (1275°F). The sorbent retains both strength and chemical activity with multiple cycles. The high oxygen and low temperature initiation allows the sorbent to be regenerated in a very small reactor.

## Introduction

Combined cycles (combinations of a gas turbine and a steam bottoming cycle) are an efficient power generation technology, while coal is the lowest-cost fuel. The combination of Coal Gasifiers and Combined Cycles, therefore, is predicted to be the lowest-cost source of baseload electric power in the next decade. In a GCC, the sulfur and particulates are removed from the gasifier gases before they enter the turbine combustor. While  $H_2S$  (and  $COS/CS_2$ ) can be removed effectively by cooling hot gases down to near room temperature and scrubbing them with an aqueous amine solution, removing the  $H_2S$  without cooling the gases (i.e., hot gas cleanup) is more advantageous.

The leading hot gas sulfur absorbent uses a regenerable zinc oxide (ZnO) based sorbent to remove the  $H_2S$  and other sulfur compounds from the hot coal gases. The zinc absorbs  $H_2S$ , forming zinc sulfide (ZnS), which is then regenerated with oxygen (air). This process releases the sulfur as a concentrated stream of  $SO_2$ . The  $SO_2$  can be converted into sulfuric acid or sulfur, or it can be reacted with calcium carbonate to form calcium sulfate (gypsum). The sorbent may be operated in a fluidized bed reactor, transport reactor, or moving bed reactor.

TDA Research, Inc. (TDA) is developing sorbents suitable for moving-bed and other types of reactors.

Under one contract, TDA is evaluating 3 to 5 mm sized sorbents for moving bed reactors ("A Long Life ZnO-TiO<sub>2</sub> Sorbent"). Under a second contract ("A Novel Desulfurization Sorbent") we are

evaluating 50 to 400 micron sized sorbents suitable for fluidized bed or transport reactors.

In this paper we discuss the application to the Moving-Bed reactor. A schematic of a moving bed system with the production of sulfuric acid from the  $\text{SO}_2$  is shown in Figure 1. Two reactors are utilized with the sorbent moving between the absorber and regenerator. The particle size is large (i.e., 3 to 5 mm = 3000 to 5000 micron).

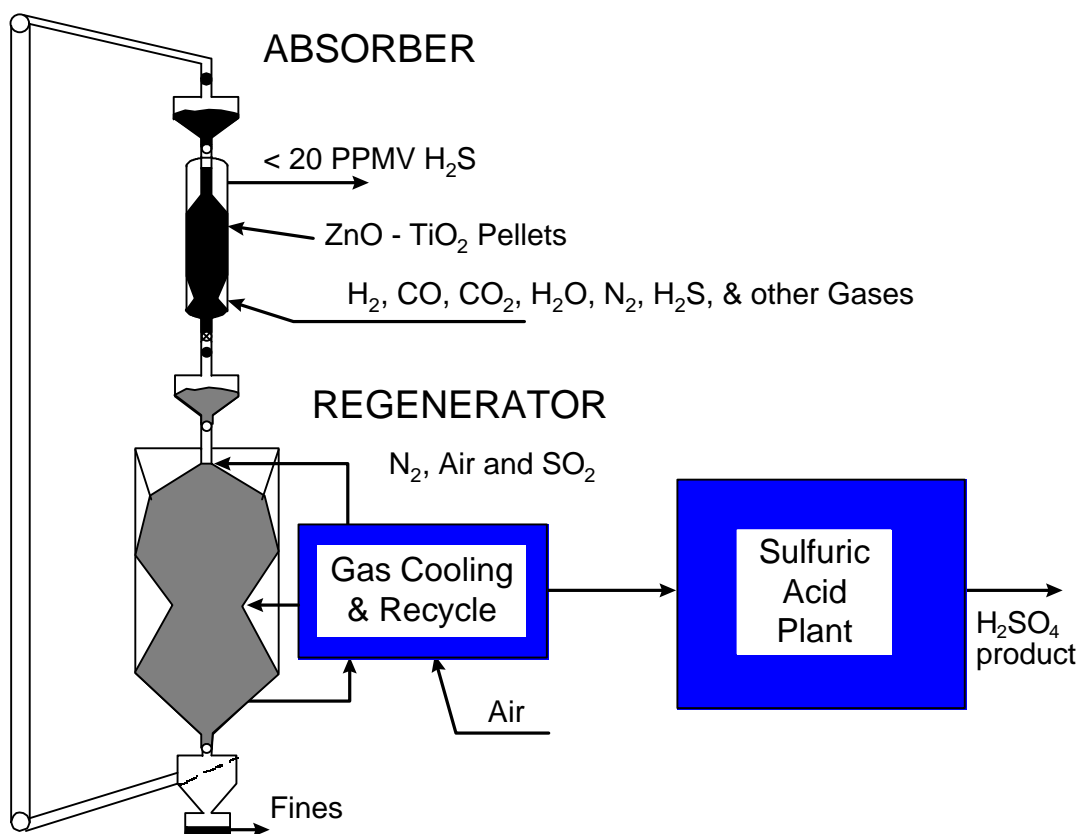


Figure 1. Moving bed reactor system.

ZnO has a high affinity for  $\text{H}_2\text{S}$  and produces a very clean gas stream. Unfortunately, the life of many ZnO-based sorbents is very limited, especially in fixed and moving bed reactors. The molar volume of the  $\text{ZnS}$  is 50% greater than that of  $\text{ZnO}$ . During regeneration some zinc sulfate can form, which can occupy more than 250% of the volume of the original  $\text{ZnO}$ . Prior to returning to the absorber, the zinc sulfate is decomposed and returns the sorbent to its original oxide form. The zinc atoms thus move substantially during absorption (to  $\text{ZnS}$ ), to regeneration (to  $\text{ZnO}$  and some  $\text{ZnO} \cdot 2\text{ZnSO}_4$ ), and finally back to the oxide ( $\text{ZnO}$ ). This repeated expansion and contraction of the sorbent as it is cycled causes many sorbents to spall (i.e., break into small pieces), which eventually destroys the sorbent (Jung et al. 1992, Mei et al. 1993). Because of the high sorbent loss rate, fresh sorbent must be continually added which in turn increases the cost of sulfur removal; substantial cost reductions could be achieved by making a more durable sorbent.

## Objective

The objective of this work was to develop and test long-life sorbents for hot gas cleanup. Specifically, we measured the sulfur loading at space velocities typically used for absorption of  $\text{H}_2\text{S}$  and regenerated the sorbent with diluted air for multiple cycles. Based on the experimental results, we prepared a conceptual design of the sorbent-fabrication system, and estimated the cost of sorbent production and of sulfur removal.

## Technology

In order to make a sorbent pellet capable of holding large amounts of sorbent without being destroyed by the absorption-regeneration process, TDA has developed a new sorbent structure with the following characteristics: 1) it is very strong, 2) it allows the sorbent to expand and contract freely without disrupting the pellet structure, 3) it allows the  $\text{H}_2\text{S}$  to diffuse quickly into the interior of the pellet, and 4) it can contain very large amounts of sorbent without spalling.

TDA prepared sorbents and evaluated them for moving bed applications. Last year (Copeland et al. 1996) we reported on a spall resistant sorbent. This year we improved our sorbent formulation and modified the regeneration procedure. We improved our attrition resistance to better than 98% while retaining high chemical activity and sulfur loadings.

We selected one sorbent formulation which was made by Norton to TDA's specifications. This sorbent, identified as TNT-MB for TDA and Norton - Moving-Bed, is a zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) with improved resistance to spalling.

Previous work in zinc ferrite has shown a tendency for the sorbent to spall (Jung et al 1992) (i.e., to break into small pieces when exposed to the regeneration gases). Krishnan et al. (1991) also reported that the zinc ferrite can make iron carbon and accumulated carbon during cycling. However, Krishnan et al (1991) also reported that "Carbon deposition rate exceeds the rate of removal by *steam*, and hence carbon is likely to accumulate on the sorbent". Since the Moving-Bed system regenerates the sorbent with oxygen, the limitation imposed by regenerating solely with steam does not apply.

Fortunately, previous work by Cook et al. (1992) has shown successful application of a zinc ferrite sorbent in a moving bed (i.e., at the pilot plant facility in Schenectady, NY). Initially their tests were run with a low regeneration temperature (less than  $1200^\circ\text{F}$ ,  $649^\circ\text{C}$ ). Sulfate was formed which was carried into the absorber in the next cycle. Sulfate formation can also cause spalling of the zinc ferrite. However, when the regenerator exit temperature was greater than  $1200^\circ\text{F}$  ( $649^\circ\text{C}$ ), the sulfate was almost completely eliminated, and a small quantity of sulfide (about 2% sulfur as sulfide with very low levels of sulfate) remained in the sorbent when leaving the regenerator.

Although zinc ferrite was shown to be a successful sorbent in a moving bed, the interest in sorbents in 1992 was toward the higher temperature absorption. Gangwal and Gupta (1991) reported: "zinc ferrite sorbents were found to be limited to  $550^\circ\text{C}$ " ( $1022^\circ\text{F}$ ) during absorption and the emphasis shifted to research on zinc titanate and related type sorbents. However, the moving bed absorber at Tampa Electric is designed to operate at  $900^\circ\text{F}$  ( $482^\circ\text{C}$ ) and thus zinc ferrite can be used at the temperature anticipated without concern.

TDA assembled a team to evaluate, produce, and test sorbents for moving-bed reactors. The team members are TDA, Norton Chemical Process Products Corporation (Norton), and the Institute of Gas Technology (IGT). TDA defined the sorbents to be evaluated and conducted multiple cycle screening tests in our fixed bed reactors. Norton produced the sorbent by techniques representative of commercial production. All pellets used in the tests described herein

were from a 2 ton batch produced by Norton; Table 1 describes the properties of this sorbent. TNT-MB has more than the minimum sulfur capacity required for the moving bed system [ $> 7.3$  lb (sulfur) per  $\text{ft}^3$  bed] and adequate attrition resistance ( $97.8\% = 2.2\%$  loss).

Table 1. Properties of TNT-MB.

● 2 ton lot: rotary kiln fired
● Bulk Density = $1.35 \text{ g/cc} = 84.2 \text{ lb/ft}^3$
● Dia. = $0.143 \text{ in} = 3.65 \text{ mm}$
● L/D = 1.32
● ASTM D5757-95 loss = 2.2%
Max. Sulfur = 12.8% (wt) (by chemical analysis)
● 9.7 lb (sulfur) per $\text{ft}^3$ bed

TDA has completed all of the required tests of the DOE test protocol. DOE-FETC performed the 10 cycle tests without  $\text{SO}_2$  required under a Cooperative Research and Development Agreement (CRADA) agreement with TDA. This CRADA included 10 cycles at  $900^\circ\text{F}$  sulfidation temperature and an additional, limited  $3 \frac{1}{2}$  cycle scoping experiment. The required 25 cycles with 10%  $\text{SO}_2$  in the regeneration gases at 5 atm were completed at IGT. TDA followed up these tests by conducting a low temperature sulfidation study which mirrored the CRADA work done by FETC, except all 10 sulfidation cycles were conducted at  $600\text{-}700^\circ\text{F}$  with no inlet  $\text{SO}_2$  in the regeneration. This paper presents the results of the tests on TNT-MB of 10 low ( $600\text{-}700^\circ\text{F}$ ) temperature sulfidation cycles at TDA and 25  $900^\circ\text{F}$  sulfidation cycles at IGT.

## Low Temperature Sulfidation

All low tests were run using a simulated Texaco gas composition (Texaco gas stream, 20 atm pressure, and a space velocity of  $2000 \text{ h}^{-1}$  with 1.2% inlet  $\text{H}_2\text{S}$ ). However inlet gas temperature was reduced to  $600^\circ\text{F}$  -  $700^\circ\text{F}$  for all 10 sulfidations. TDA experienced some water flow control problems and, as a result, data from TDA was grouped according to which of the two common flow rates we observed. Data from sulfidations that contained water flow rates which fell outside the two categories

Table 2. Gas compositions in sulfidation and regeneration.

	Absorption		Regeneration	
Carbon Dioxide	12.2	%	-	%
Carbon Monoxide	35.8	%	-	%
Hydrogen	26.8	%	-	%
Hydrogen Sulfide	1.2	%	-	%
Nitrogen	5.9	%	96.0	%
Oxygen	-	%	4.0	%
Sulfur Dioxide	-	%	-	%
Water - desired	18.1	%	-	%
range	10.0 - 19.5			
Pressure	20	atm.	7	atm.
Space Velocity	2000	$\text{h}^{-1}$	2000	$\text{h}^{-1}$
Temperature	600-700	$^\circ\text{F}$	700-1300	$^\circ\text{F}$

reported were removed. All regenerations at TDA were conducted without SO<sub>2</sub> in the inlet gas, 2000 h<sup>-1</sup> space velocity, and 7 atm pressure.

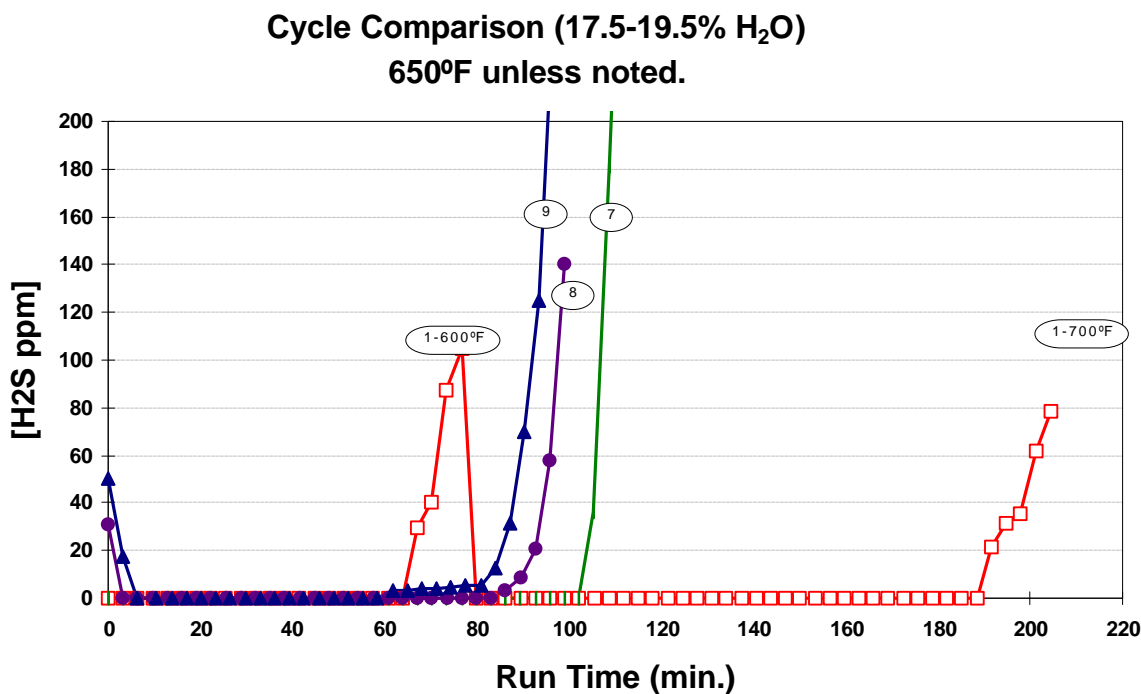


Figure 2. Low temperature sulfidations with 18% water.

Starting absorption and regeneration conditions are outlined in Table 2. All regenerations at TDA were conducted without SO<sub>2</sub> in the inlet gas, 2000 h<sup>-1</sup> space velocity, and 7 atm pressure with an initial bed and inlet gas temperature of 700°F.

Figure 2 and Figure 3 detail the breakthrough times associated with the two main water flows (17.5 - 19.5 % H<sub>2</sub>O and 10.0-12.0% H<sub>2</sub>O) recorded in the TDA low temperature sulfidation study. As can be seen, the water flow had a major impact on breakthrough time of these sorbents, with higher water concentrations leading to shorter the breakthrough times. Thus irregularities in water flow could easily contribute to some of the scatter in breakthrough times recorded. In addition to the curves shown, one run had complete pump failure ½ hour into the sulfidation and the resulting breakthrough time was in excess of 3 hours (180 min+) at 650°F.

Cycles 1 and 10 were initiated at 600°F (315°C) and increased to 700°F (371°C) as the lower temperature reached its breakthrough point. However, water flow after 600°F breakthrough in cycle 10 was again out of our specifications so that only the 600°F breakthrough time was reported. As the temperature increased in the bed, the H<sub>2</sub>S in the outlet again decreased due to better absorption at higher temperatures until it reached its breakthrough point for that elevated temperature. The first cycle at FETC was conducted similarly. However, experimental design dictated only ½ hour at the 600°F set point, followed by raising the bed to 700°F and running for 125 total minutes. Observed H<sub>2</sub>S levels were < 1 ppm at the completion of 30 minutes, and around 180 ppm at the completion of the 125 minute test.

Figure 4 presents the measured temperatures on the 10<sup>th</sup> sulfidation. Initially there is a small temperature rise, due to absorption of H<sub>2</sub>S, since this thermocouple is near the inlet. As the absorption wave passes the thermocouple, the temperature returns to the inlet temperature. However, when the bed is heated to 700°F, the temperature first rises due to the heating by the oven and then continues to rise with time. The second portion of the temperature rise is due to the exothermic water gas shift reaction.

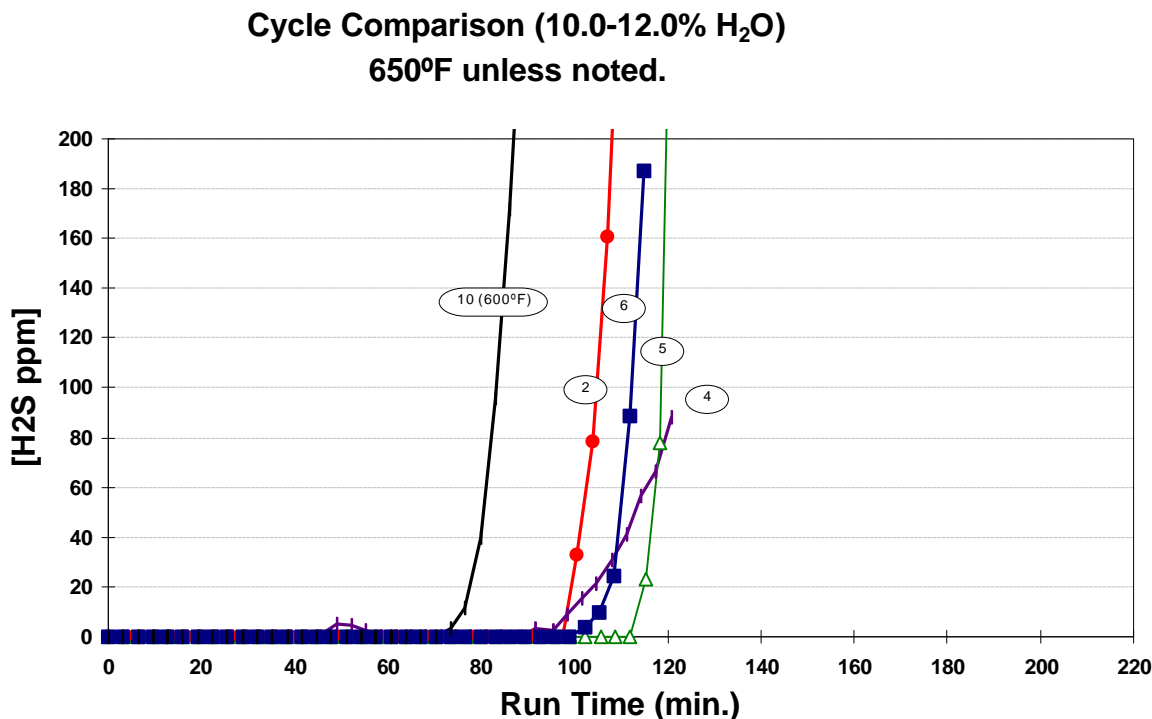


Figure 3. Low temperature sulfidations with low water content.

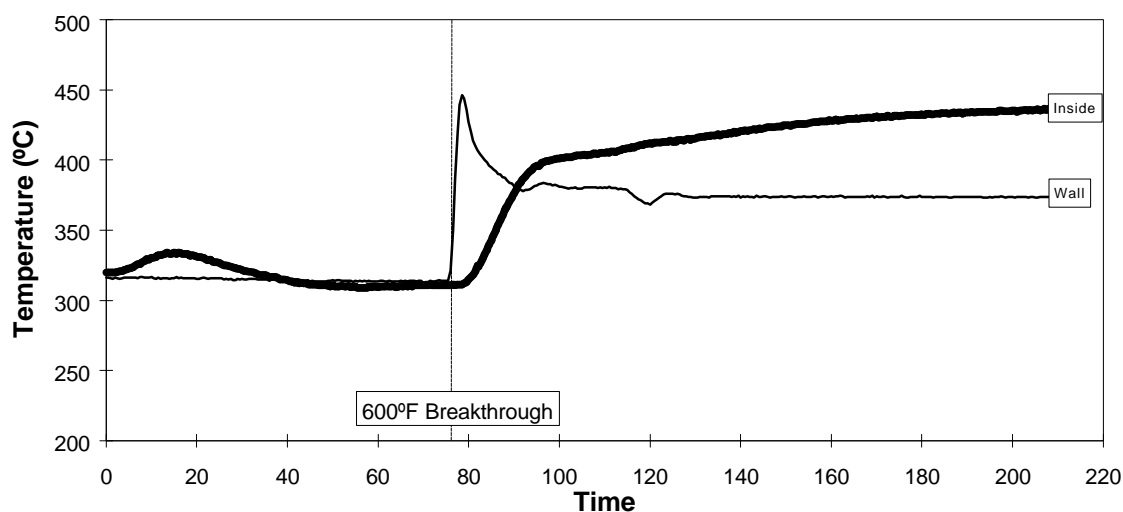


Figure 4. Tenth cycle temperature (low temperature sulfidation at TDA)

Based on measured gas compositions we measured a shift from CO to H<sub>2</sub> with a corresponding increase in CO<sub>2</sub> (see Figure 5). Within the accuracy of the measurements the total carbon in the inlet gas equaled the total carbon in the exit gas. The water-gas shift reaction was still catalyzed at 700°F, although not to the same extent as the 900°F case; but in the 600°F case very little, if any, shift was observed.

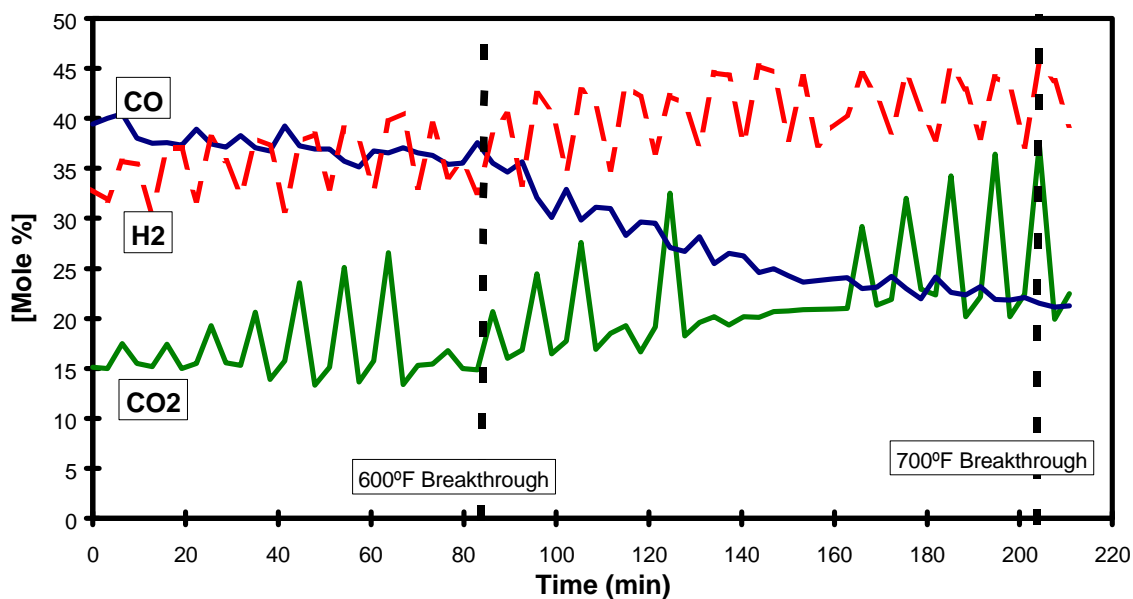


Figure 5. Gas exit composition in first low temperature sulfidation at TDA.

## Micro-balance Testing a 900°F

The TBT-MB sorbent activity was measured in a micro-balance at the Institute of Gas Technology. Three samples were tests 1) fresh, 2) samples from the top (exit) and 3) sample from the bottom (inlet) from the material used in the ten cycle baseline tests that were conducted for TDA at DOE-FETC (the break through tests were reported in last years paper)(see Copeland et al. 1997). The fresh sorbent was exposed at 900°F to the sulfidation gas containing 1.2% H<sub>2</sub>S with the gas compositions for simulated Texaco gases (Table 2). Figure 6 presents the results. The fresh material was exposed for 125 minutes (i.e., from 30 minutes where the all gases but H<sub>2</sub>S were flowing to stabilize the reactor) to 155 minutes where the test was terminated.

All three samples reached the same weight increase 4.75%, which indicates a sulfur absorption of 9.5 g sulfur per 100 g for fresh material. The fresh material had the slowest weight increase (i.e., sulfur absorption). The samples from the bottom (inlet) from the 10 cycle tests had the fastest rate of absorption and the samples top (exit) was between the other two.

### Sorbent: TNT-MB (114) FRESH Top, & Bottom after 10 cycles

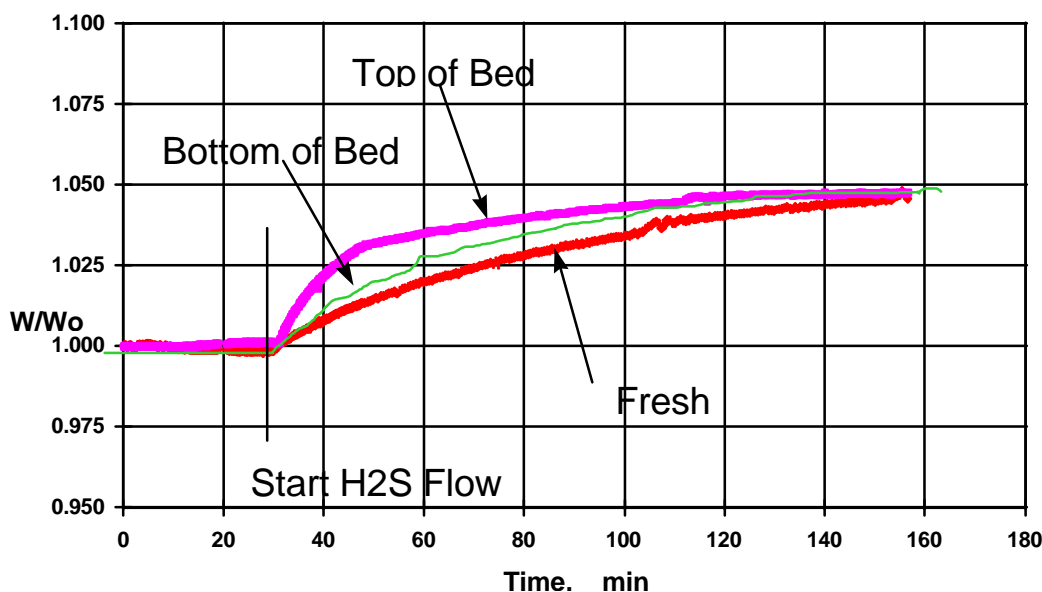


Figure 6. Micro-balance data from IGT. (20 atm, 1.2% H<sub>2</sub>S).

The data in Figure 6 indicate that the TNT-MB sorbent does not loose activity with cycling. Rather the sorbent clearly improves its activity with cycling, a result which is consistent with the breakthrough testing conducted at TDA.

## 900°F Sulfidation

TNT-MB is a non-spalling zinc ferrite which was exposed to 25 sulfidations and 24 regenerations with up to 10% SO<sub>2</sub> in the regeneration gas. Figure 7 presents the breakthrough H<sub>2</sub>S concentration as a



function of time for the 24<sup>th</sup> sulfidation; the other breakthroughs have a similar appearance. For the first 30 minutes (i.e., -30 to 0) no H<sub>2</sub>S is flowing but H<sub>2</sub>S appears in the outlet; during this period the H<sub>2</sub>S is being generated by reductive regeneration of sulfates remaining in the sorbent at the end of the regeneration (see following section on regeneration). This effect continues for another 30 minutes until all of the sulfate has been decomposed. The H<sub>2</sub>S then drops to a low level and remains there until about 75 minutes and then it slowly rises until it reaches 270 ppm at 125 minutes.

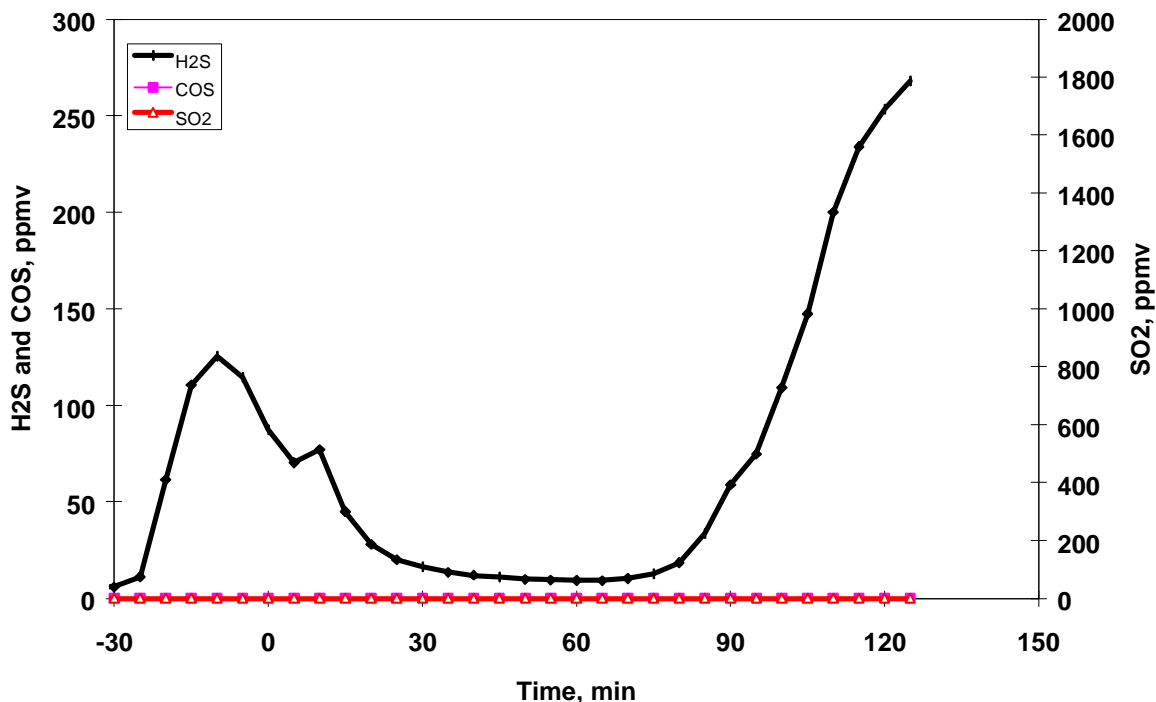


Figure 7. 24<sup>th</sup> 900°F sulfidation.

The sorbent is sensitive to the quantity of oxygen in the regeneration gas (i.e., integral of the O<sub>2</sub> flow rate over time) and the regeneration procedures (see following section). TDA found it necessary to modify the test procedures during the 24 regenerations to minimize the oxygen supplied during regeneration. Figure 8 presents the measured ratio of oxygen consumed to sulfur absorbed for each of the 25 sulfidations. When properly control the following sulfidation can removed sulfur for the required period of time as shown in Figure 7.

In the first 10 regeneration's the  $O_2$  flow was very high ( $> 2.2 O_2/S$ ) leading to excess sulfate formation and very high temperatures in the bed during the next sulfidation. TDA reduced the oxygen flow and ( $\sim 1.6 O_2/S$ ) but this lead to incomplete oxidation of the sulfides and early breakthrough of the sorbent. Raising the  $2.2 O_2/S$  ratios to about 1.8 produced a sorbent which had adequate oxidization of the sulfide without excessive sulfate formation. Unfortunately, experimental difficulties did not allow us to maintain the desire oxygen flow and the  $O_2/S$  dropped back to 1.5 in cycles 20-22 and lead to early breakthrough, increasing the oxygen flow back to the desired level improved the breakthrough time to the value shown in Figure 7.

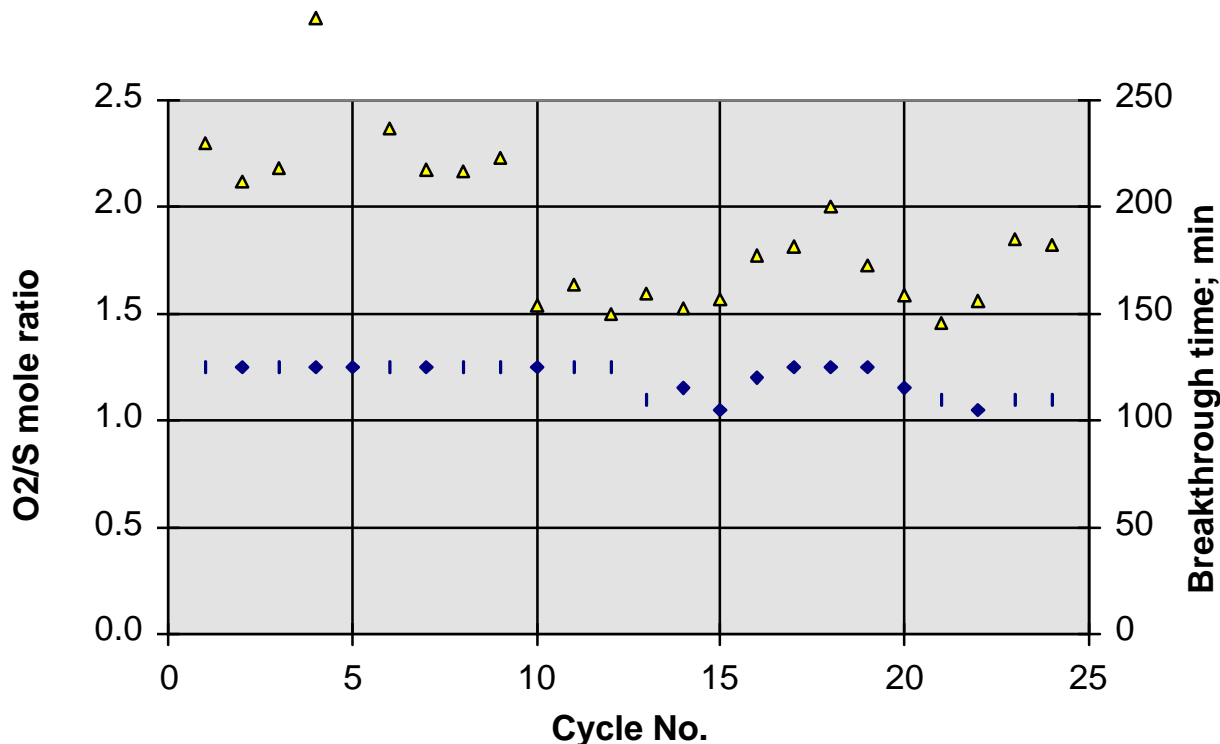


Figure 8. 25 sulfidations at 900°F.

The 25<sup>th</sup> sulfidation was conducted, but samples were removed from the bed following the 24<sup>th</sup> regeneration and thus the bed size and breakthrough time are not consistent with the other cycles and the data are not shown to avoid confusion.

### Regeneration

Cook et al. (1992) regenerated zinc ferrite successfully when the exit temperature exceeded 1200°F (see Figure 9). TDA studied the data from Cook et al. (1992) and conducted thermodynamic analysis of why this result was achieved. TDA found that above 1200°F, the iron sulfates were not thermodynamically stable, even in the presence of both oxygen ( $O_2$ ) and  $SO_2$  and at pressures up to 7 atm. We regenerated TNT-MB in a moving bed reactor using this proven approach to minimizing sulfate.

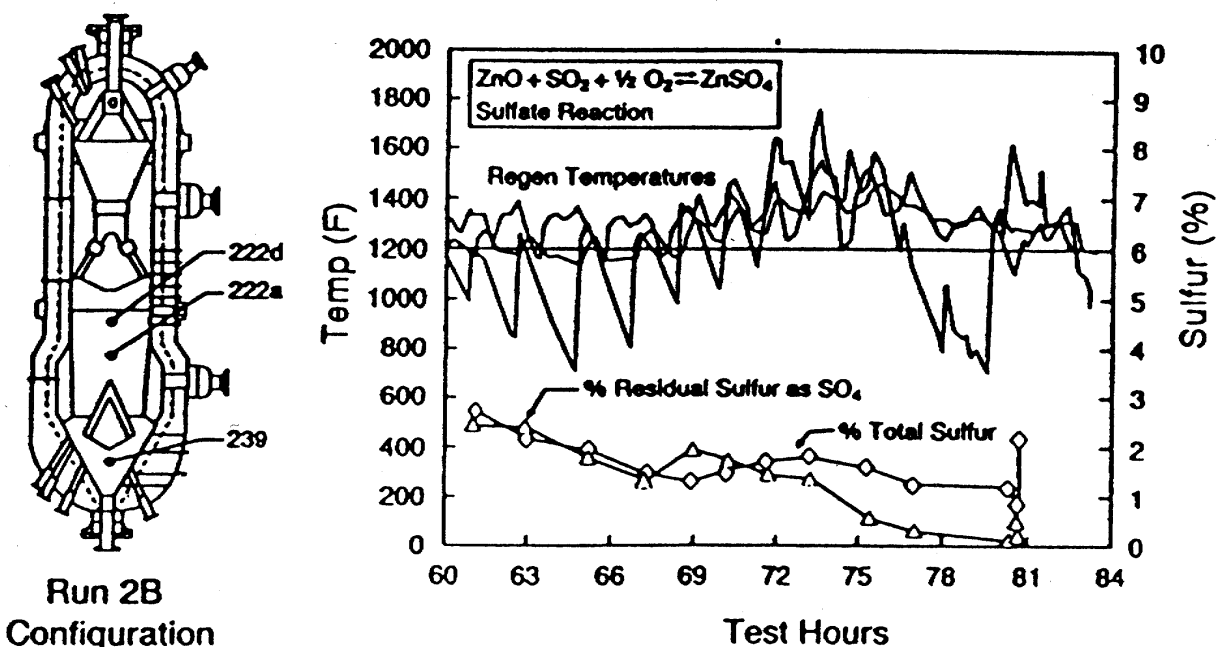


Figure 9. GE HGCU regenerator performance run 2B, zinc ferrite (Cook et al. 1992).

#### Description of the Regeneration in a Moving Bed Reactor

Figure 10 illustrates the preferred conditions to regenerate TNT-MB in a moving bed. The regenerator uses a simple co-flow reactor with only one inlet and one exit. Cook et al (1992) used a dual inlet regenerator in the tests of zinc ferrite. Our sorbent will initiate regeneration with 4% O<sub>2</sub> and with the sorbent and inlet gas at 700°F (TDA conducted some regenerations with 600°F initial sorbent and inlet gas temperature). We used the self heating of the oxidation of the sorbent to raise its temperature to over 1250°F, and allow a small heat loss from the reactor. Without any heat loss the sorbent and gases

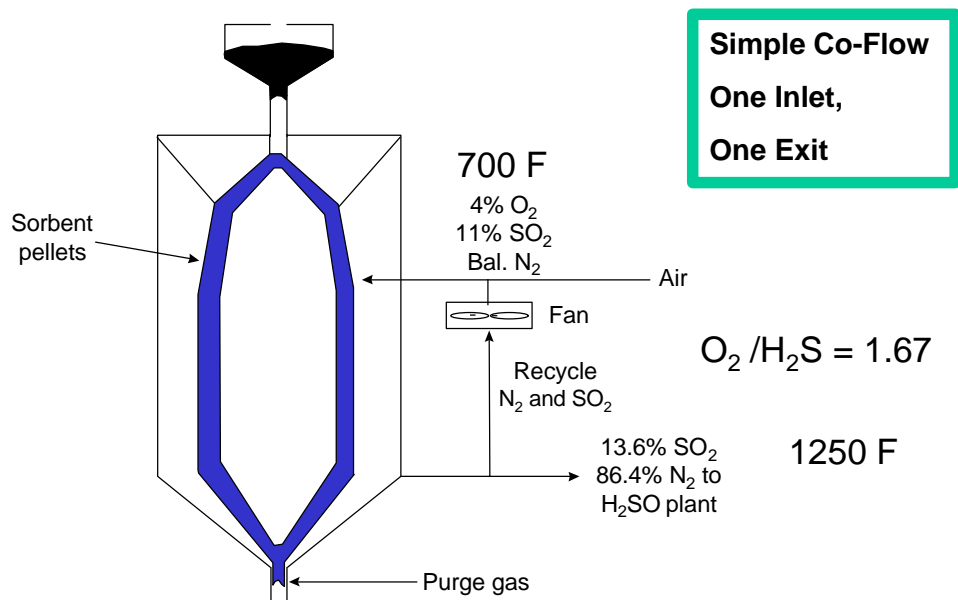


Figure 10. Moving bed regenerator with TNT-MB

would exit at 1295°F (702°C). The control of the reactor was relatively simple. Inlet temperature was controlled by the cooling of the recycle gases and exit temperature was controlled to 1250°F ± 50°F by the air flow added to the reactor.

Theoretically 1.67 moles of oxygen are required to fully oxidize fully sulfided zinc ferrite. As shown in Figure 10. TDA calculated the maximum SO<sub>2</sub> concentration leaving the reactor as 13.6%. In tests at TDA, we measured a ratio of 1.7 moles O<sub>2</sub> per mole of H<sub>2</sub>S absorbed.

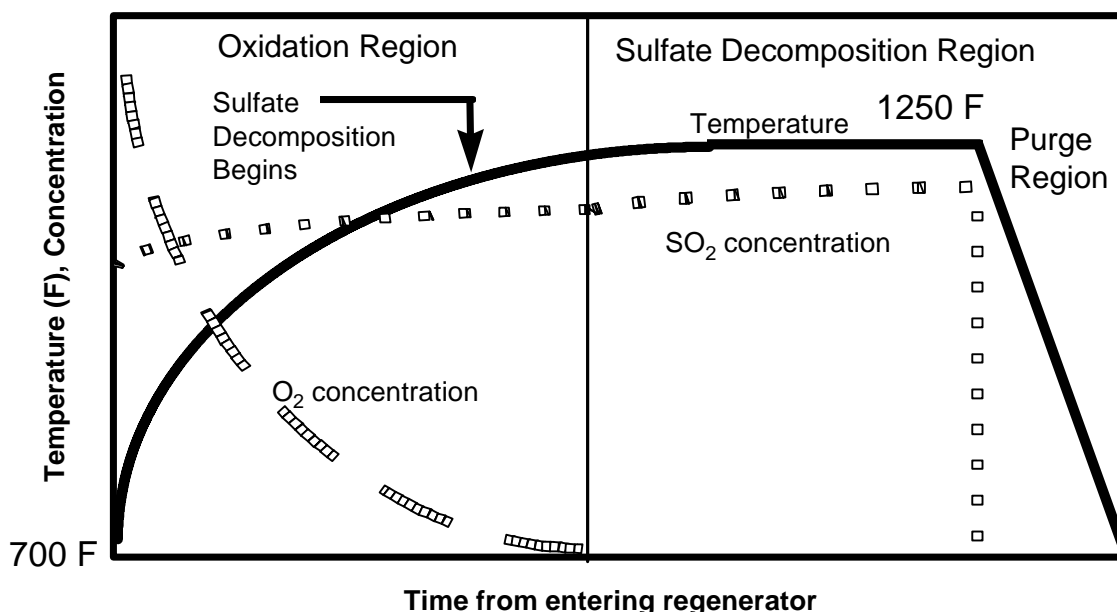


Figure 11. Gas composition and temperature in regenerator

Figure 11 illustrates the temperature and gas concentrations in the sorbent as it moved down the reactor. Initially, the sorbent was rapidly heated due to the oxidation of the sulfide. Simultaneously the oxygen concentration was reduced and the SO<sub>2</sub> concentration was increased. During this period some sulfate was formed by the reaction of oxygen, SO<sub>2</sub>, and iron oxides. Since the amount of sulfate formed was a function of time, it was very desirable to minimize the time the sorbent was less than 1200°F. TDA preferred the high oxygen concentration (4%) with a low inlet temperature and a single inlet to minimize the time. This approach minimized the quantity of sulfate formed and the tendency of the sorbent to spall.

When the temperature reached 1200°F sulfate decomposition began even in the presence of oxygen and SO<sub>2</sub>. Finally, a point was reached when essentially all of the oxygen was consumed and the temperature reached 1250°F. TDA preferred that the sorbent remain in the bed at this high temperature for about one hour to fully decompose the sulfate and raise the SO<sub>2</sub> concentration to its maximum value. After the sorbent was regenerated it entered the nitrogen purge at the bottom of the reactor. This step cooled the sorbent and purged SO<sub>2</sub> from the gas space before returning the sorbent to the sulfiding reactor.

TDA recognized that the testing of the TNT-MB was done in a small scale fixed bed reactor and that the conditions of a real moving bed could not be exactly duplicated. We therefore defined two regions

of operation for the tests: 1) Oxidation Region where the sorbent was self heating to 1250°F, and 2) Sulfate Decomposition where the sulfate was decomposing at 1250°F. In more recent low temperature tests carried out at TDA, we inserted a third stage to this regeneration procedure which we called the oxidative sulfate decomposition stage. In this stage the bed temperature was raised to 1200°F and a reduced (1.0-2.0%) oxygen flow was introduced. This was done immediately following oxygen breakthrough with all temperature ramps done under nitrogen only. This stage was meant to simulate the conditions just downstream from the oxidation front, which contained reduced oxygen in the presence of increased temperature. This step was followed by the normal anaerobic sulfate decomposition stage described above.

The regeneration were conducted at a spaced velocity at both of the two testing sites; the inlet conditions were as follows:

- TDA: 7 atm, 700°F, no SO<sub>2</sub> - 4.0% O<sub>2</sub>, balance N<sub>2</sub>
- IGT: 5 atm. 700-750°F, up to 10% SO<sub>2</sub>, to 3 to 4% SO<sub>2</sub>, balance N<sub>2</sub>

#### Regeneration in a Fixed Bed Reactor without SO<sub>2</sub> at TDA

A typical regeneration at TDA following a 200 min absorption is shown in Figure 12. It can be seen that a large amount a sulfate was decomposed in the ramp region and that there was significant sulfur remaining at the end of the first oxidation. Also to be noted, there were few sulfates remaining as this second stage oxidative decomposition reached oxygen breakthrough, and total regeneration time (minus the temperature ramp) was still only slightly longer than the corresponding absorption. Sulfur balance was good, although we suspect that the temperature in the oxidative decomposition region got a little too high at higher bed locations leading to the formation of some zinc sulfates. This was corrected in later regenerations but could have affected subsequent absorption characteristics.

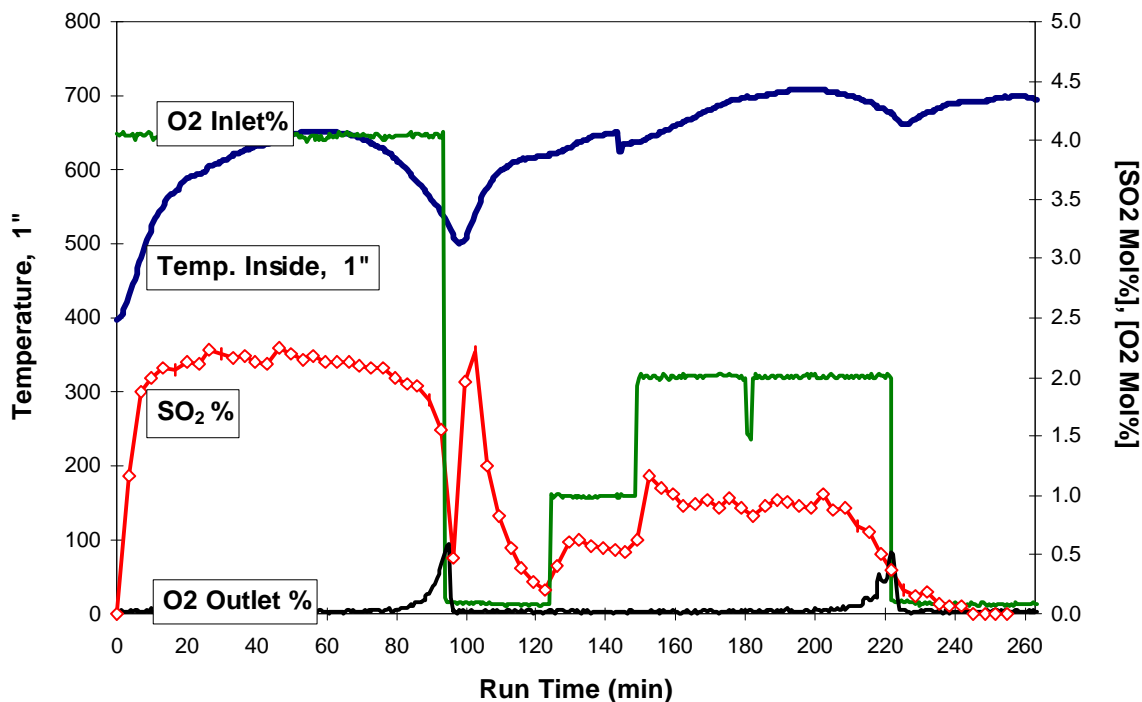


Figure 12. Run time.

Figure 12 presents the measured temperatures and  $\text{SO}_2$  and  $\text{O}_2$  concentrations in this three region regeneration approach at TDA. Initially the temperature near the inlet (e.g., the 2 inch location) was low. As the oxidation of the sorbent near the inlet proceeded, it warmed the pellets in the fixed bed reactor at the downstream locations (i.e., 4 inch and 6 inch locations). The heating of the pellets by low oxygen containing gases effectively increased the temperature of some sulfided material before it was oxidized, and caused a rapid increase in the peak temperature. The inlet oxygen was reduced after about one hour to maintain a peak temperature of less than  $1300^\circ\text{F}$ . The reduced  $\text{SO}_2$  concentration at one hour was due to the reduced inlet oxygen content. After about 1.5 hours, the oxygen broke through and approached its inlet value. Since most of the sulfide had been oxidized away, the temperatures in the reactor declined. The oxygen supply was then terminated; and the temperature of the reactor was ramped to  $1250^\circ\text{F}$  without any oxygen in the inlet gas. Since there was no  $\text{SO}_2$  in the inlet gas, the sulfate decomposition began at less than  $1200^\circ\text{F}$  as shown by the increase in  $\text{SO}_2$  concentration at 1.75 hours.

Excluding the time which was required to heat the sorbent to  $1250^\circ\text{F}$  following the oxidation region, the regeneration required a total time of about 120 minutes following a 125 minute absorption. The oxidation regeneration required 60 minutes and sulfate decomposition 60 minutes. The regeneration thus could be conducted in about the same volume as the sulfidation since both are operated at the same space velocity.

However, the regenerator at Tampa Electric Company (TECo) had about twice the volume as the Sulfiding reactor. If the regeneration gases were introduced at the top inlet at TECo, the sorbent would be sitting at  $1250^\circ\text{F}$  for about 3 hours after the oxidative regeneration. To minimize the potential loss of surface area and activity of the sorbent from this long period at high temperature, we

preferred that our TNT-MB be regenerated by introducing gas at the middle location with no gas, or gas without oxygen, introduced at the top location (see Figure 10).

#### Regeneration in a Fixed Bed Reactor with SO<sub>2</sub> at IGT

All of the regeneration at IGT were conducted 5 atm. 700-750°F, up to 10% SO<sub>2</sub>, to 3 to 4% SO<sub>2</sub>, balance N<sub>2</sub>. The DOE test protocol required that the first three cycles be conducted with small quantities of SO<sub>2</sub> in the inlet to simulate the start up of a moving bed reactor. In the fourth cycle the SO<sub>2</sub> inlet was to be controlled to achieve a 10% SO<sub>2</sub> concentration in the outlet and was remained the same for the remaining 24 regenerations.

Figure 13 presents the measured O<sub>2</sub> and SO<sub>2</sub> in the inlet and exit during the fourth regeneration at IGT. Initially, 4% O<sub>2</sub> was supplied to the reactor but to prevent excessively high temperatures in the reactor, the O<sub>2</sub> concentration was reduced to 3.1% after 27 minutes. The O<sub>2</sub> continued at 3.1% inlet until the exit concentration reacted 1% O<sub>2</sub> and which time the oxygen was turned off and the bed heated to 1200°F. When the bed reacted 120°F, the oxygen was increased to 2% inlet and SO<sub>2</sub> inlet increased to 10%. After a few minutes the O<sub>2</sub> began to breakthrough and the oxygen was turn off.

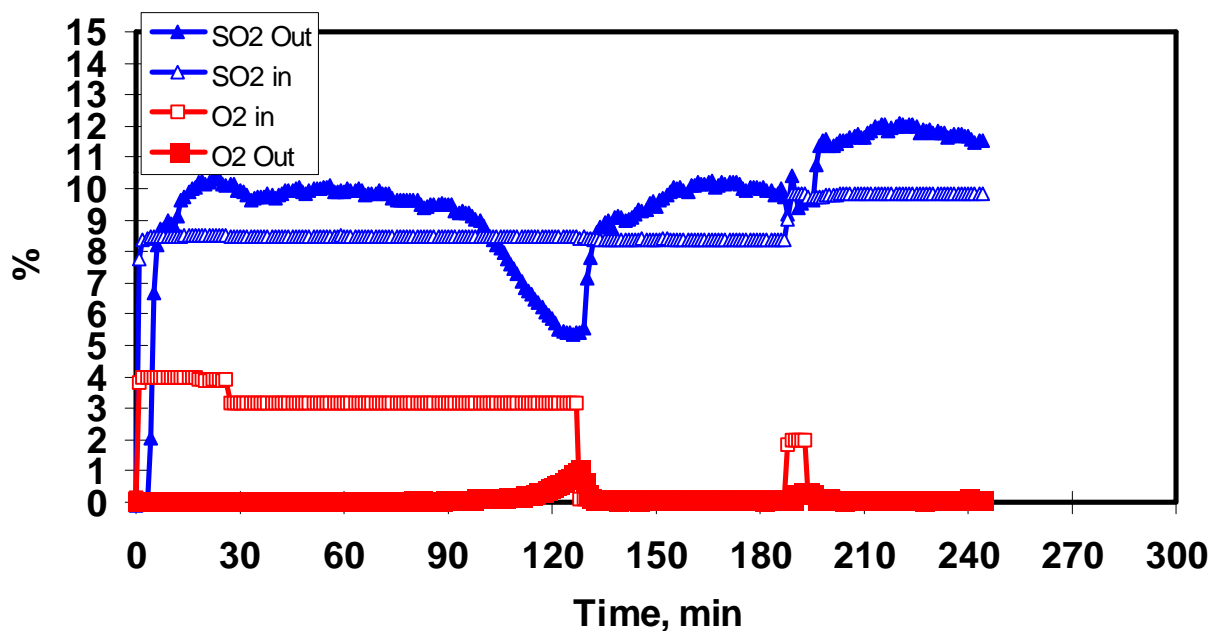


Figure 13. Cycle 4 Sulfate Formation at IGT.

The inlet SO<sub>2</sub> was initially set at 8.5% and held constant until off oxygen was turn off; when it was raised to 10%. After a short start up time the SO<sub>2</sub> in the outlet reached 10% ± 0.5% and remained in that range until about 90 minutes. Then the SO<sub>2</sub> in the outlet decreased 5%, substantially less than the inlet, even though O<sub>2</sub> was being consumed. The sorbent was clearly making large quantities of sulfate during the first 127 minutes and a large fraction of the O<sub>2</sub> was being consumed to make sulfate. Overall this regeneration consumed about twice as much oxygen as would be required to oxidized the zinc and iron sulfides to zinc ferrite.

Additional evidence of sulfate formation is seen in the time aft 127 minutes; the SO<sub>2</sub> outlet with or

without oxygen present exceeds the inlet  $\text{SO}_2$  (i.e., 8.5% inlet  $\text{SO}_2$  increases to ~10% without oxygen present; and after 195 minutes 10%  $\text{SO}_2$  increased to ~12%). Since the outlet  $\text{SO}_2$  was substantially higher than the inlet at the end of the cycle, not all of the sulfate was decomposed. We also observed that fifth absorption had a very large initial temperature spike due to the oxidation of the sulfate and the release of  $\text{SO}_2$ , which also indicate that the sulfate was fully decomposed.

Recognize these factors, TDA modified the regeneration procedure to limited the quantity of oxygen supplied. Figure 14 presents the  $\text{O}_2$  and  $\text{SO}_2$  in the inlet and exit for the final regeneration procedure. The  $\text{O}_2$  initially was supplied at 3.4% and raised to 3.8% after 42 minutes to reached the maximum desired temperature in the bed. After 78 minutes the  $\text{O}_2$  was turned off and remained off for the remainder of the test. The oxygen required was only 1.8 moles of  $\text{O}_2$  per mole of  $\text{H}_2\text{S}$  absorbed during sulfidation.

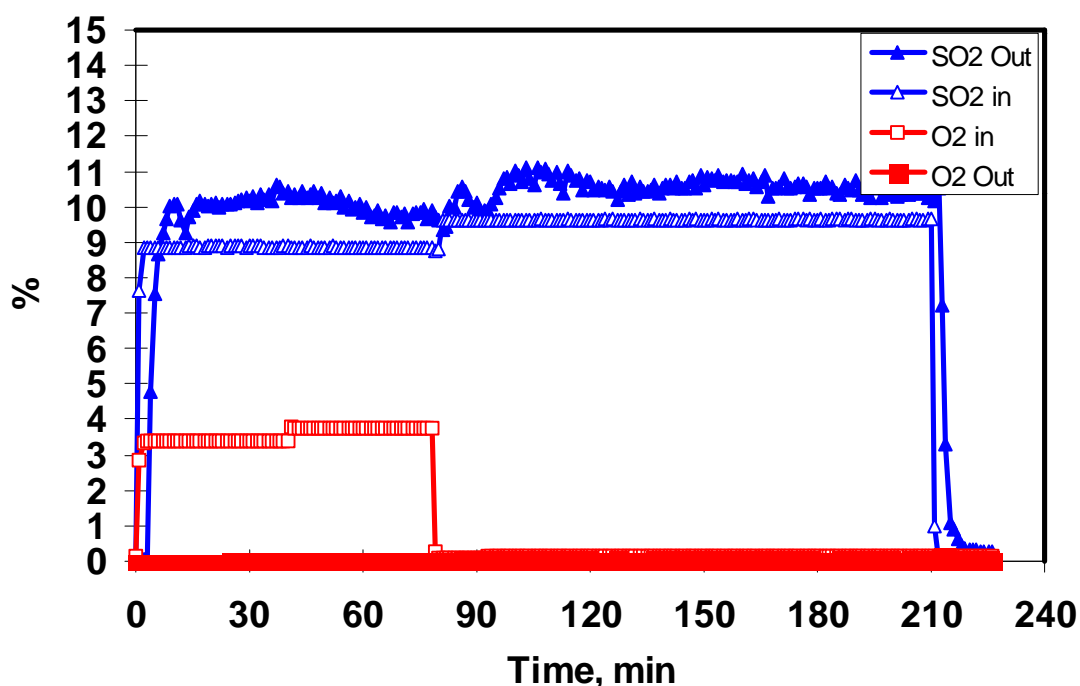


Figure 14. Sulfate Decomposition at IGT 5 atm, Cycle No. 23.

After the  $\text{O}_2$  was off, the  $\text{SO}_2$  increased to 9.5% (see Figure 14) and the temperature of the reactor was raised to 1250°F (see Figure 15). The increased time in the sulfate decomposition stage decomposed more as indicated the steady 10%  $\text{SO}_2$  after the temperature increased to 1250°F, indicating a release of 0.5%  $\text{SO}_2$  due to sulfate decomposition.



TDA recognized that the formation of sulfate can be a problem in zinc ferrite. We conducted equilibrium analyses which showed that above 1200°F at 5 atm with small quantities of O<sub>2</sub> and 10% SO<sub>2</sub>, the iron sulfates will decompose to Fe<sub>2</sub>O<sub>4</sub> and SO<sub>2</sub> and some O<sub>2</sub> (which will be consumed by any residual sulfides). However, thermodynamically the zinc sulfate (ZnO\*2ZnSO<sub>4</sub>) is stable at all temperatures and concentrations in the reactor.

Fortunately the kinetics of the formation of zinc sulfate (ZnO\*2ZnSO<sub>4</sub>) are very slow and tests at TDA show that it does not form rapidly until the temperatures exceed 1400°F. For that reason we limited the maximum temperature in the reactor to 1300°F and adjusted oxygen flow to the temperature below 1300°F (to minimize zinc sulfate formation) but required that the oxidization reach a temperature above 1200°F (to decompose iron sulfates). In a moving bed reactor the desired affect is achieved as evidenced by the measurements of Cook et al (1992)(see Figure 9).

In a fixed bed reactor the inlet region initially mimics the moving bed (for about the first 30 minutes at the 1" location of Figure 15) and the bed autothermally heats itself to about 1300°F with the oxidization of the sulfides regenerating them to the oxides. Unfortunately, the cool gases entering the reactor then cool the inlet sorbents, and the inlet region is now exposed for an extended period of time where there is little to no sulfide, high levels of O<sub>2</sub> and SO<sub>2</sub> and the temperature is less than 1200°F. Under those conditions large quantities of iron sulfates form, specifically in the inlet region but to a lesser extend in the other regions of the bed also where the temperature is less than 1200°F. While this effected is limited in a moving bed (the sorbent only increases in temperature as shown in Figure 10) in a fixed bed reactor the iron sulfate formation regions is unavoidable; TDA defined the second stage (and sometimes third stage) to simulate the hot sulfate decomposition stage inherent in a moving bed.

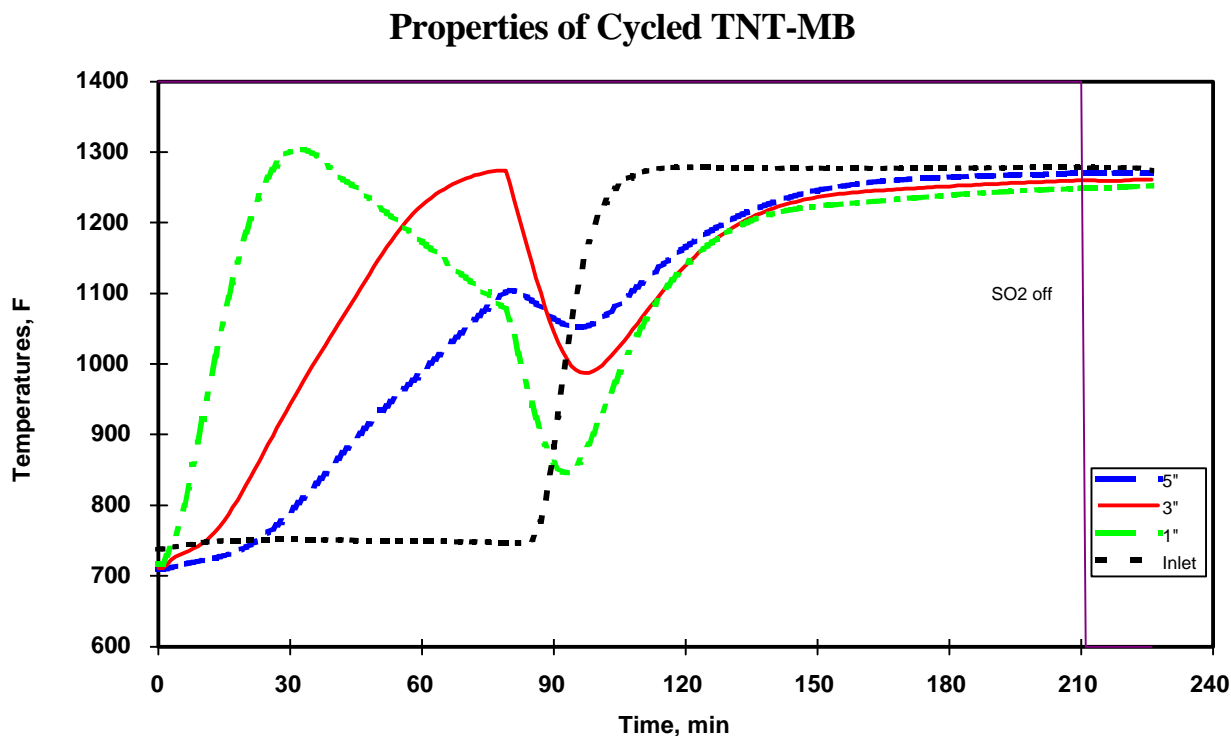


Figure 15. 23<sup>th</sup> Regeneration at IGT.

### Following Low Temperature Cycling without SO<sub>2</sub> in the Inlet

Following the 10<sup>th</sup> sulfidation and the 10<sup>th</sup> regeneration at TDA, samples were taken from the bottom (inlet) and the top (exit) of the sorbent bed. Table 3 presents the measured properties of TNT-MB lot 298, from these tests.

Table 3. Properties of TNT-MB before and after 10 low temperature sulfidations.

	Attrition	Crush	Surface	Porosity	Sulfur	Carbon
	wt%	Strength lbs.	Area m <sup>2</sup> /g	g/cc	%	%
<b>As Sintered</b>	2.22	31.3	2.55	.2395	0.46	0.02
<b>10A - Outlet</b>	1.99	33.4	2.30	.2309	2.40	< 0.05 *
<b>10A-Inlet</b>	1.99	29.9	3.63	.1643	11.71	< 0.05 *
<b>10R - Outlet</b>	1.63	30.4	2.55	.2175	2.00	< 0.05 *
<b>10R - Inlet</b>	1.50	33.3	2.53	.2262	2.13	< 0.05 *

\* Limit of Detection

The fresh TNT-MB contained a small amount of sulfur which was sulfate remaining at the end of the natural gas firing of the sorbent. After the 10<sup>th</sup> regeneration at FETC, very small levels of sulfate sulfur remained in the sorbent (0.30% and 0.27% respectively), indicating that the sulfate decomposition region was achieving the desired effect. Sulfate analysis was not conducted on the samples from TDA's 10 cycle low temperature study. Higher levels of sulfur remained in the sorbent following regeneration at both TDA and FETC (2.0% - 2.8%), similar to the levels measured by Cook et al. (1992) in their regeneration in a real moving bed (1.2% total sulfur, 0.2% sulfate sulfur).

High levels of sulfur were also measured following the 10<sup>th</sup> low temperature sulfidation at TDA (up to 11.7%). This value was lower than that obtained following the 10<sup>th</sup> absorption at FETC as would be expected with a lower temperature absorption, with a shorter breakthrough time.

The ASTM attrition loss was measured by TDA for the fresh material (1.8% wt. loss after 30 minutes). After 4 regenerations with SO<sub>2</sub> in the inlet of the regeneration gas, the attrition improved (1.3% loss). After 10 regenerations without added SO<sub>2</sub> the attrition loss was only 0.87% wt at the inlet and 0.64% from the exit locations. In comparison, the allowable loss was 5% after 25 cycles. Clearly, the data indicates that we have the potential to surpass this requirement, but we need to complete the 25 cycle tests with SO<sub>2</sub> before a definitive conclusion can be reached.

Zinc ferrite is known to form small quantities of carbon (Krishnan et al. 1991) and potentially can make iron carbide. We measured the total carbon content of the TNT-MB following the 10<sup>th</sup> sulfidation and regeneration. The limit of detection of the samples at TDA was 0.05% wt carbon. All of the cycled samples contained less than 0.05% wt carbon, indicating that carbon did not accumulate with cycling

### Following 900°F Cycling with up to 10% SO<sub>2</sub> in the Inlet

Table 4 presents the measured properties of the TNT-MB before and after the 25 cycle tests at IGT. The primary difference in the two tests was the high level of SO<sub>2</sub> in the inlet gas (up to 10%) which increases both the rate and quantity of sulfate formation. The formation of the sulfate increases the

volume, which is then lost when the sulfate decomposes (either thermally in the regenerator and reductively at the start of the next sulfidation). The change in solid volume inside the pellets affects the structure of the sorbent, weakening it. The loss of strength reduces the attrition resistance from 1.7% fresh loss to 3.1% to 4.8% after the 25<sup>th</sup> sulfidation (Note: the attrition loss in Table 4 were measured at FETC and thus the fresh attrition loss was slightly different from that measured at TDA).

Table 4. Sorbent Properties after 25 cycles at IGT.

	Attrition	Surface Area	Porosity	Sulfur	Sulfate sulfur	Carbon
	wt%	m <sup>2</sup> /g	cc/g	wt%	wt%	wt%
As Sintered (fresh) (max sulfur)	1.67	2.55	0.2395	0.46 (10.36)	0.27 (0.42)	0.02
25A - Inlet (bottom) (max sulfur)	3.06	3.73	0.1752	9.27 (9.81)	1.40 (1.20)	<0.01
25A-Outlet (Top) (max sulfur)	4.78	2.63	0.1990	7.19 (12.79)	1.35 (0.74)	<0.01
24R - Inlet (bottom)	7.14	4.40	0.1910	5.49	2.82	<0.01
24R - Outlet (top)	3.30	2.19	0.1966	7.59	1.99	<0.01

The formation of sulfate during regeneration also affected the amount of sulfide remaining in the sorbent at the end of regeneration. Where Cook et al (1992) were able to regenerate in a real moving bed (1.2% total sulfur, 0.2% sulfate sulfur), the fixed bed tests at IGT did not achieve complete regeneration (i.e., 5.5 to 7.6% sulfur of which 2.0 to 2.8% was sulfate). Thus, the fixed bed with SO<sub>2</sub> in the inlet does not simulate the real moving bed; which is not surprise since a fixed bed is clearly not a moving bed. TDA recognized the limitation but given the constraints and lack of an available moving bed, the procedures were developed to simulate as well as can be in a fixed bed reactor.

As in the tests at TDA and the CRADA at FETC, carbon content of the sorbent was very low after cycling, indicating that the accumulation of carbon in not a problem in this sorbent.

## Application

TNT-MB is a NON-SPALLING Zinc Ferrite Sorbent which is being tested for application to a moving bed reactor system. The testing to date shows that the sorbent can easily meet the requirements for sulfur loading, ASTM attrition loss, and operating conditions required. In addition, the sorbent is able to operate at relatively low temperatures @600°F: > 60 minutes to breakthrough; @ 700°F: > 3 hours to breakthrough, and @ 900°F: > 7 hours to breakthrough. TNT-MB offers the potential to reduce the costs of future moving bed hot gas cleanup systems. Since our regenerator requires only a single inlet, the complexity of the regeneration gas flow is reduced which reduces capital costs. Also, our regenerator could be half the size of the current Teco regenerator, further reducing capital costs.

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